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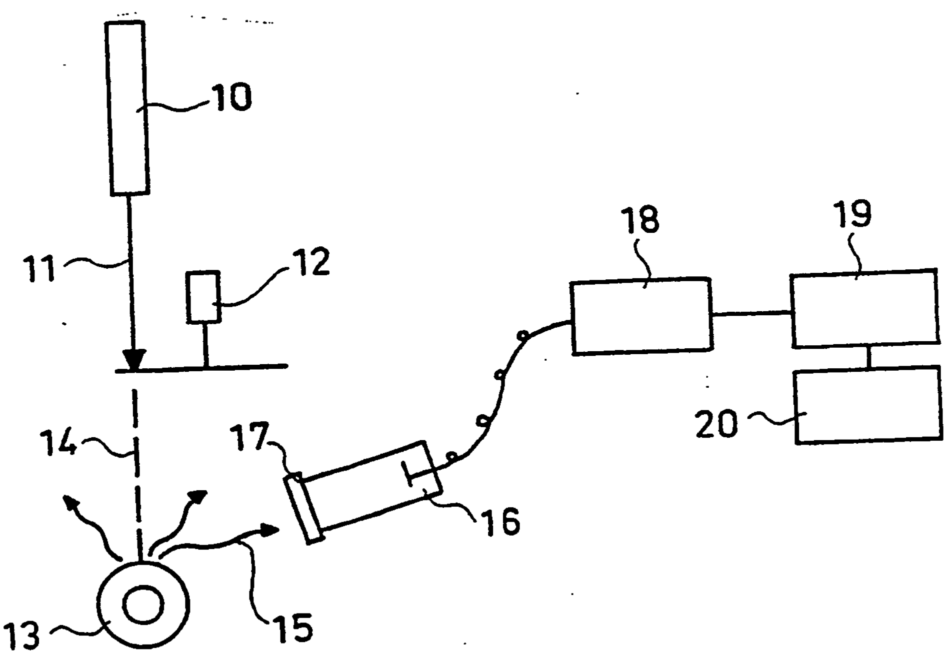
(54) Title: PROCEDURE AND MEANS FOR MEASURING THE DEGREE OF CROSS-LINKING OF PLASTICS

(57) Abstract



Procedure and means by which the degree of cross-linking of primarily PEX plastic can be measured when manufacturing cable insulation or piping of polyethylene plastic. It has been observed in the invention that the intensity of the fluorescence (15) of PEX plastic increases as a function of the degree of cross-linking. The means comprises a laser (10) for focussing a modulated laser light beam (14) producing fluorescence on the sample (13), and an electronic light detector (16) for detecting the fluorescent radiation (15) produced by the sample (13). In front of the light detector (16) is placed a filter (17) absorbing the exciting light, whereby the electronic signal from the light detector (16), which is proportional to the degree of cross-linking, may be carried to requisite electronic amplifiers (18) and other signal processing systems (19, 20) to output the degree of cross-linking of the sample (13). The means of the invention is suitable for on-line measurement in an extrusion machine.

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Procedure and means for measuring the degree of cross-linking of plastics

The present invention concerns a procedure and a means for measuring the degree of cross-linking of plastics, in particular of polyethylene, continuously without touching the sample. As is well known, plastics have a great number of different uses. Polyethylene in particular has several quite significant technical applications, of which may be mentioned the insulation of high tension cables, and water and sewer pipes. The chemical and electrical durability of polyethylene plastics is excellent and the mechanical strength in itself is also at least satisfactory. If polyethylene is used for instance as material for a hot water piping, it is obvious that it should tolerate temperatures higher than 100°C, and it should be durable otherwise as well. When the temperature rises over 80°C, polyethylene, or PE, tends to soften unless it is so-called cross-linked polyethylene or PEX, the temperature endurance of which is considerably in excess of 100°C.

Polyethylene products are manufactured in the so-called extrusion process, in which the plastic mix in molten state is pressed through an orifice to its final shape, e.g. to become a tube or an insulation upon a cable. Thereafter, it is subjected to heat treatment, or vulcanizing, at which process in the polyethylene are formed transversal molecular bonds in great number between carbon atoms (cross linkages), which add to its strength and durability so that it may be used for instance as a water pipe. When a pipe is manufactured by extrusion, it has been exceedingly difficult heretofore to know whether the formation of cross-links has been adequate. From the production has been taken a sample which has been taken to the laboratory, whence the degree of linking has then been learned several hours later.

The amount of vulcanizing of PEX plastics is indicated by its degree of cross-linking. A water pipe, for instance, is required

to be 70% cross-linked at a minimum, to be usable in its intended use. The degree of cross-linking of PEX is currently measured by various chemical and physical methods, the most important of which are believed to be the so-called steeping method and the infra-red method, in both of which, the starting of cross-linking is measured as peroxide residual quantity. These procedures are laboratory methods and are not applicable in one-line control, and they are used only after the product has been completed, so that a sample could be taken for the laboratory.

Since PEX plastics are manufactured by continuous extrusion, it is obvious that it is impossible to stop the production for sampling. Thus, there is both a technical and an economical need to develop a meter able to measure the degree of cross-linking of PEX directly during the production in accordance with the on-line principle. One could then be assured that the quality of the end product is continuously uniform and up to quality specifications. The meter need not measure the absolute degree of cross-linking: it is sufficient if it monitors the changes of the degree of cross-linking, whereby the quality could be maintained above a given threshold.

The object of the present invention is a continuously operating, non-contact on-line meter for measuring the degree of cross-linking of PEX (and other plastics). The means of the invention directly measures the degree of cross-linking and outputs it electronically; if desired, the degree of cross-linking can be obtained in digital form. This implies however that the means has to be calibrated with a known specimen. Since the apparatus does not measure the absolute degree of cross-linking, it has to be calibrated to actuate an alarm when the obtained electronical signal falls below a given pre-set value. Even in this form, the meter would be an excellent guarantee of the quality of the production. It has been found that in its present form the meter would be particularly appropriate for monitoring the water pipe production and for monitoring cable coatings. In tests that have been carried out, the means has performed well with high-density plastic, but also

with low-density plastics the means has been tried out successfully. In high voltage cables also PEX with chalk filler is used, and in the experiments carried out the means has worked well. On the other hand poor results have been obtained in the case of cables with soot filler.

The means of the invention is based on the observation that the intensity of fluoresence of PEX plastic increases with increasing degree of cross-linking. In the tests that have been carried out it has been found that non-cross linked PE plastic fluoresces very little; however, the intensity increases almost linearly as a function of the degree of cross-linking. The spectrum of fluorescence also seems to change, but monitoring of the intensity appears to give the best result.

It has further been found that as exciting light laser light should be used, because only from a laser is obtained an adequate intensity for reliable observation of the fluorescence. Furthermore, the spectral distribution of laser light is narrow enough to bring out the desired fluorescence spectrum. When tests with conventional fluorescence lamps were carried out, the measurements were quite more cumbersome because, in the first place, the intensity of an ordinary fluorescence lamp is weak and variable, the focusing of the light beam derived therefrom is inconvenient, while guiding the light beam therefrom to the desired point is not easy, its spectral distribution is wide and requires filtering, and finally the service life of fluorescence lamp is much shorter than that of laser light sources. Utilization of a UV fluorescence lamp may be contemplated in laboratory conditions, but in industrial environment it may be impractical. Thus, the use of a laser is recommended. The monitoring of narrow laser light is also rather convenient beside a production machine.

In the means of the invention, the PEX specimen under examination is illuminated with a HeCd laser light beam through a rotating chopper. Hereby, the PEX specimen is hit by light which is intensity-modulated lightly modulated at a given frequency f. The PEX

plastic begins under effect of the excitation light to fluoresce, whereby the fluorescence occurs at the same frequency f as the incoming modulated light. By monitoring the intensity of fluorescence and variations, the variations in degree of cross-linking are in this manner found out. Since the fluorescence occurs at a given frequency f, it is easy to construct an electronic amplifier which is tuned to the same frequency f as the fluorescence detected by a light detector. At the same time, the interfering lights occurring at other frequencies are filtered out in the amplifier. The intensity of fluorescence is monitored with a light detector, which may be either a photomultiplier tube or a semiconductor detector. It is essential that in front of this light detector is mounted an optical filter which efficiently absorbs the specific wavelength of the exciting laser light, whereby only the fluorescent light can pass through.

The best results have been obtained with light from a HeCd laser, although an argon laser or a UV-type laser, for instance, may be used. When cross-linking is taking place, a plurality of crossing bonds between carbon atoms are formed. The creation of a bond means the creation of a new energy level. As the cross-linking increases, the number of energy levels correspondingly increases, and the number of the fluorescent levels increases. The fact that different plastics may fluoresce is in itself known in the art, but that the fluorescence increases as a function of the degree of cross-linking is new and constitutes the object of the present invention. The principle is applicable even in the instance in which chalk has been added to the plastic as filler, but not when there is soot in it.

Regarding the state of the art, let the U.S. Patent No. 4,107,245 be acknowledged, in which the degree of cross-linking of polyethylene is measured by adding to the plastic certain chemical dyes, the colour properties of which change as the degree of cross-linking increases. Alternately, it is possible to add to the plastic a kind of stained calibration tape from the colour changes of which it is possible to deduce the magnitude of the degree of

cross-linking. Firstly, one may note that the dyeing ingredient in question must be uniformly distributed in the plastic for the measurement to be reliable. Secondly, if a stained tape is used, the plastic object has to be cut open so as to reveal the tape. Finally, it is likely that customers are not interested in plastic displaying colour variations. The present invention is free from these drawbacks; on the contrary, the degree of cross-linking of PEX plastic is already revealed with raw material combinations as used in present practice. Furthermore, the accuracy of measurement of the invention is good: compared with the chemical steeping method constituting the standard, the accuracy is better than +3%. The correlation coefficient is then higher than 0.94 in the requisite measuring range.

The German Patent No. 2 928 306 includes an arrangement in which the optical characteristics especially of granular material are measured while the sample is in motion in a sample chamber. In the claims of this patent, the detection of fluorescence is also presented, but it has no association with cross-linking.

The present invention is characterized by the circumstances stated in the claims.

The invention is described in detail, with reference being made to an advantageous embodiment of the invention presented in the figures of the drawing attached, to which the invention is not, however, intended to be exclusively confined.

Fig. 1 illustrates the formation of fluorescence and its observing.

Fig. 2 shows in perspicuous manner the principle of construction of the means of the invention.

Fig. 1 clarifies the formation of fluorescence in the specific case that the narrow spectral distribution of a laser is used for exciting light. With UV lamps not equally good results are achieved. In Fig. 1, the spectral line 1 represents the exciting light, which

is extremely narrow for the reason that it comes from a laser. The spectrum 2, again, represents the fluorescence spectrum that is formed, and which invariably lies at a longer wavelength than the exciting light. The fluorescence is formed immediately without delay. The absorption spectrum 3 of the filter which removes the exciting light absorbs efficiently the exciting light in front of the light detector, whereby the detector sees only the fluorescence. Since the spectral distribution of the laser is very narrow, only a minimal fraction of the fluorescent light is masked by the exciting light.

Fig. 2 elucidates the design and the principle of operation of the means of the invention. A light beam 11 coming from the laser 10 is so modulated by means of a chopper 12 that the sample 13 is hit by a light beam 14 having the said modulation frequency f. There are also electro-optical designs stabilizing the light intensity, known in prior art, but they shall not be described in this connection since they are no essential from the point of view of the present invention. The fluorescent light 15 modulated at frequency f, produced by the cross-linking, is observed with a light detector 16, in front of which is placed a filter 17 absorbing the exciting light, and this filter itself must not emit any fluorescence. After the light detector 16 are placed electronic detectors and amplifiers 18 produced in a technique known in itself in the art, and tuned to the frequency f. The output of the detector 18, which is a certain function of the degree of cross-linking, may be taken e.g. to a computer on microprocessor basis or to other requisite control or alarm apparatus 19 and 20. For the detector 18 may also be used a phase detector known in itself in the art, while from the point of view of the inventive idea this is not essential.

The means of the invention can be used to measure on line the cross-linking of PEX plastic in cable machines, in PEX tube machines, but equally on machines and apparatus manufacturing various boards, bands or PEX coatings.

Claims

1. A procedure for measuring continuously the degree of cross-linking of plastics, in particular of polyethylene, without touching the specimen, characterized in that on the sample (13) is focussed a light beam (14) producing fluorescence, the intensity of the fluorescent radiation (15) formed in the plastic being a function of the degree of cross-linking of the plastic.

2. A means based on the procedure according to claim 1 for measuring continuously the degree of cross-linking of plastics, in particular of cable insulations of polyethylene, characterized in that the means comprises a laser (10) for focussing a fluorescence-producing modulated laser light beam (14) in the cable-manufacturing machine on the cable, an electronic light detector (16) for detecting the fluorescent radiation (15) produced by the cable plastic, in front of said light detector (16) being placed a filter (17) absorbing the excitation light, whereby the electronic signal proportional to the degree of cross-linking supplied by the light detector (16) can be carried to requisite electronic amplifiers (18) and to other signal processing systems (19,20) to output the degree of cross-linking of the cable plastic.

3. A means based on a procedure according to claim 1 for continuous measuring of the degree of cross-linking of plastics, in particular of pipes of polyethylene, characterized in that the means comprises a laser (10) for focussing a modulated laser light beam (14) generating fluorescence in the pipe-manufacturing machine on the tube, an electronic light detector (16) for detecting the fluorescent radiation (15) produced by the pipe, in front of said light detector (16) being placed a filter (17) absorbing the exciting light, whereby the electronic signal produced by the light detector (16), proportional to the degree of cross-linking, can be carried to requisite electronic amplifiers (18) and other signal processing systems (19,20) to output the degree of cross-linking of the pipe.

4. The means according to claim 2 or 3 for continuous measurement of the degree of cross-linking of plastics, in particular of polyethylene, characterized in that the sample (13) being measured is a board, film or equivalent coating or protection made of polyethylene.

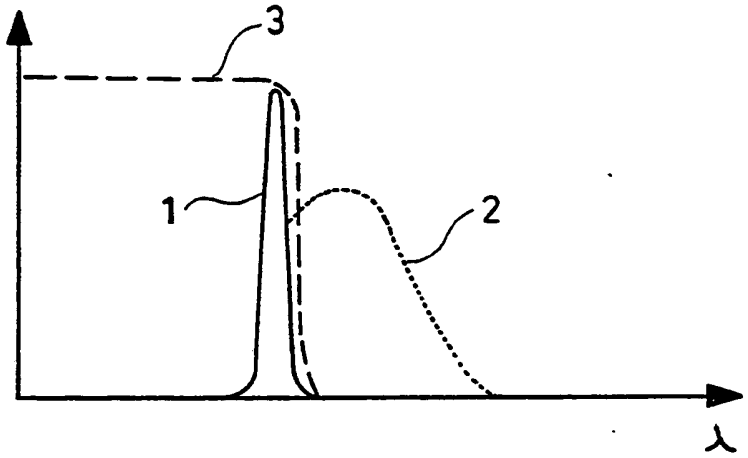

FIG. 1

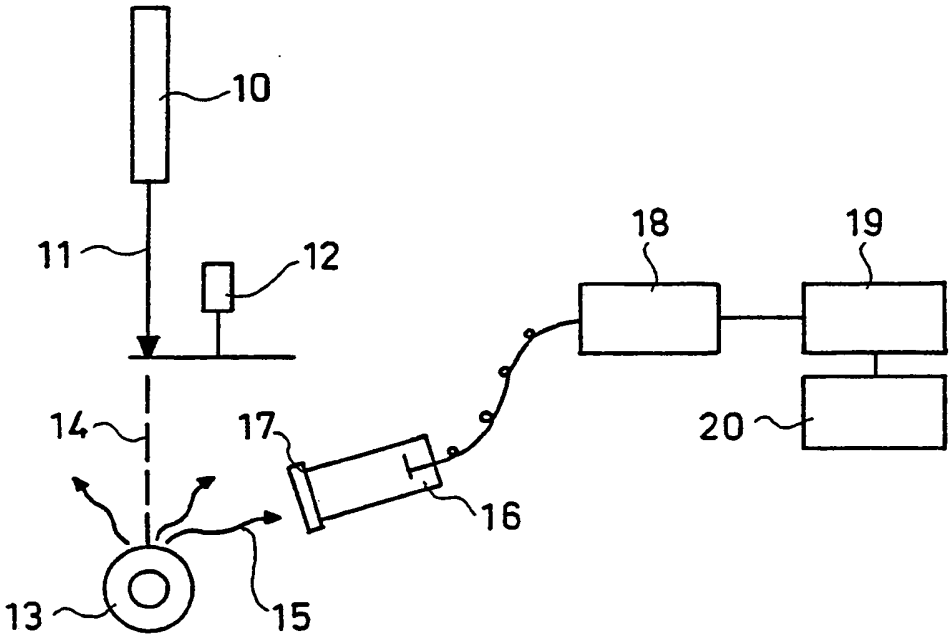

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI83/00047

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

G 01 N 21/64, 33/44, C 08 J 3/24

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC 3	G 01 N 21/33,39,62-64,86,88,89, 33/44, C 08 J 3/24
IPC 2	G 01 N 21/30-34,38,52
US CL	73:150; 250:71,71.5,219,341,562,563,572; 356:51,73.1,167,239, 342,343,430

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [5]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category [6]	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 4 208 126 (ELECTRIC POWER RESEARCH INSTITUTE) 17 June 1980	1 - 4
X	GB, A, 1 143 243 (SIEMENS-SCHUCKERWERKE AKTIENGE-SELLSCHAFT) 19 February 1969	1 - 4
X	GB, A, 1 311 932 (ENGLISH CALICO LTD) 28 March 1973	1
X	SU, A, 676 074 (AS BELO METALPOLYM) 25 February 1980	1
X	WO, A1, 81/03704 (VALMET OY) 24 December 1981 & EP, 0 053 167 AU, 72939/81	2 - 4
A	DE, A1, 2 903 879 (WIRSBO BRUKS AB) 9 August 1979	1 - 4
A	DE, B1, 2 928 306 (HOECHST AG) 9 October 1980	1 - 4

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[6] Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [3]	Date of Mailing of this International Search Report [3]
1983-08-19	1983 -08- 30
International Searching Authority [1]	**Signature of Authorized Officer** [20]
	Monica Eurenius

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
A	US, A, 4 107 245 (ALLMÄNNA SVENSKA ELEKTRISKA AKTIEBOLAGET) 15 August 1978	1 - 4